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Analysis of the results obtained for proficiency testing schemes in laboratories for food control in Institute of Public Health, Skopje, FYROM

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INTRODUCTION

Participation in proficiency testing programmes or in inter laboratory comparison is a way to demonstrate laboratory competence inside the laboratory, to the direct customer and to 3rd parties (e.g. accreditation). It also has role in improvement measurement skills (educational aspect) and is a part of quality control procedures for monitoring the validity of tests. Therefore participation in proficiency testing programmes is one of the main tasks of each laboratory for chemical testing which tends to have reliable and approved testing results.

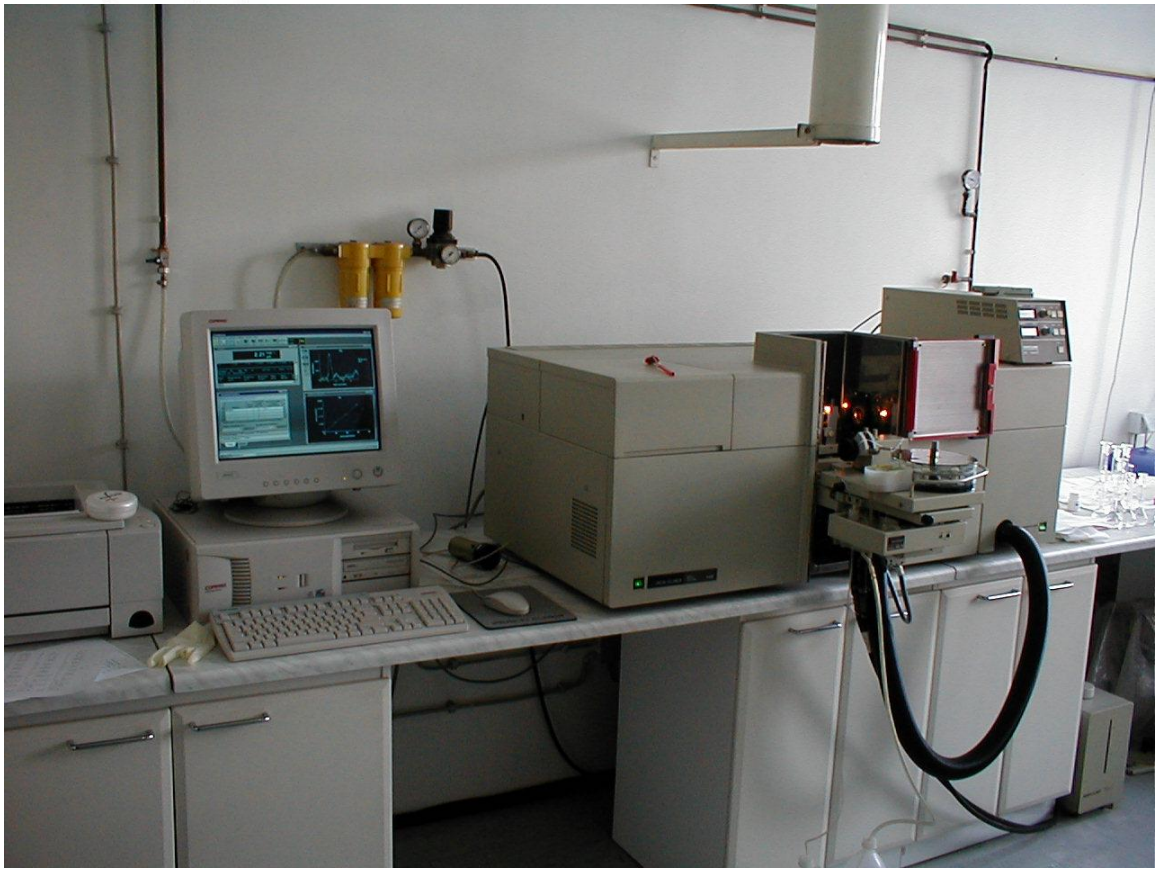
Laboratories for chemical testing of food and water in Institute of Public Health, Skopje, Republic of Macedonia have an almost one decade participation in various proficiency – testing schemes for 73 different parameters in 23 different matrixes.

The matrixes which were analyzed were: coffee cream, cream, powdered milk, yoghurt butter; cheese; oily dressing, cola drink, cabbage puree, fresh cheese, orange juice, potable water, water real sample, animal feed cereal based, fish oil, maize flour, corn flakes, minced canned fish, graham flour, synthetic food of vegetable and animal origin, homogenized canned fruit, powdered rice, dietetic product, fish soup and fresh fish.

The parameters which were analyzed were: fat content, dry matter, water content, benzoic acid, nitrate content, caffeine, saccharine, K – acesulfame., protein content, pH, citric acid, fructose, glucose, sucrose, total sugars, aflatoxins (B1; B2 G1; G2;), trihalomethanes (chloroform; bromoform; carbon tetrachloride; trichloroethene and tetrachloroethene), organophosphorus insecticides (etrimfos; fenitrothion; malathion; pirimiphos–methyl; azinphos-methyl; dichlorvos; chlorofenvinphos; parathion-ethyl; parathion-methyl; chlorpiryfos; diazinon and mevinphos), organochlorine insecticides (endrin; dieldrin; aldrin; pp'DDT; lindane; endosulfan I; endosulfan II; HCH; heptachlor; heptachlor epoxide; cis chlordane and pp'DDE), herbicides (alachlor; trifluralin; atrazine; propazine and simazine), metals (lead; cadmium; zinc; copper; chromium; iron; manganese; cobalt; nickel; mercury and arsenic), routine components in water (pH; turbidity; colour; conductivity at 20^0 C; SR phosphate; ammonium; PI; nitrate; nitrite;

sulphate; chloride; fluoride; alkalinity; total hardness; calcium; sodium; potassium and magnesium.

Providers for chemical testing of food and water were: Muva Kempten Quality Management & Laboratory Services; DRRR Deutsches Referenzbüro für Lebensmittel-Ringversuche und Referenzmaterialien; FAPAS and LEAP (UK) and The Swedish National Food Administration (NFA).



RESULTS AND DISCUSSION

I. ANALYSI OF FAT CONTENT, PROTEIN CONTENT AND DRY MATTER IN FATTY FOOD

Coffee cream, cream, powdered milk, yoghurt butter; cheese with different fat content, powdered milk with different fat content, were tested for the content of fat, protein and dry matter in 9 different samples. The number of measurements was 42.

The obtained results for Z score values are shown in figure 1.

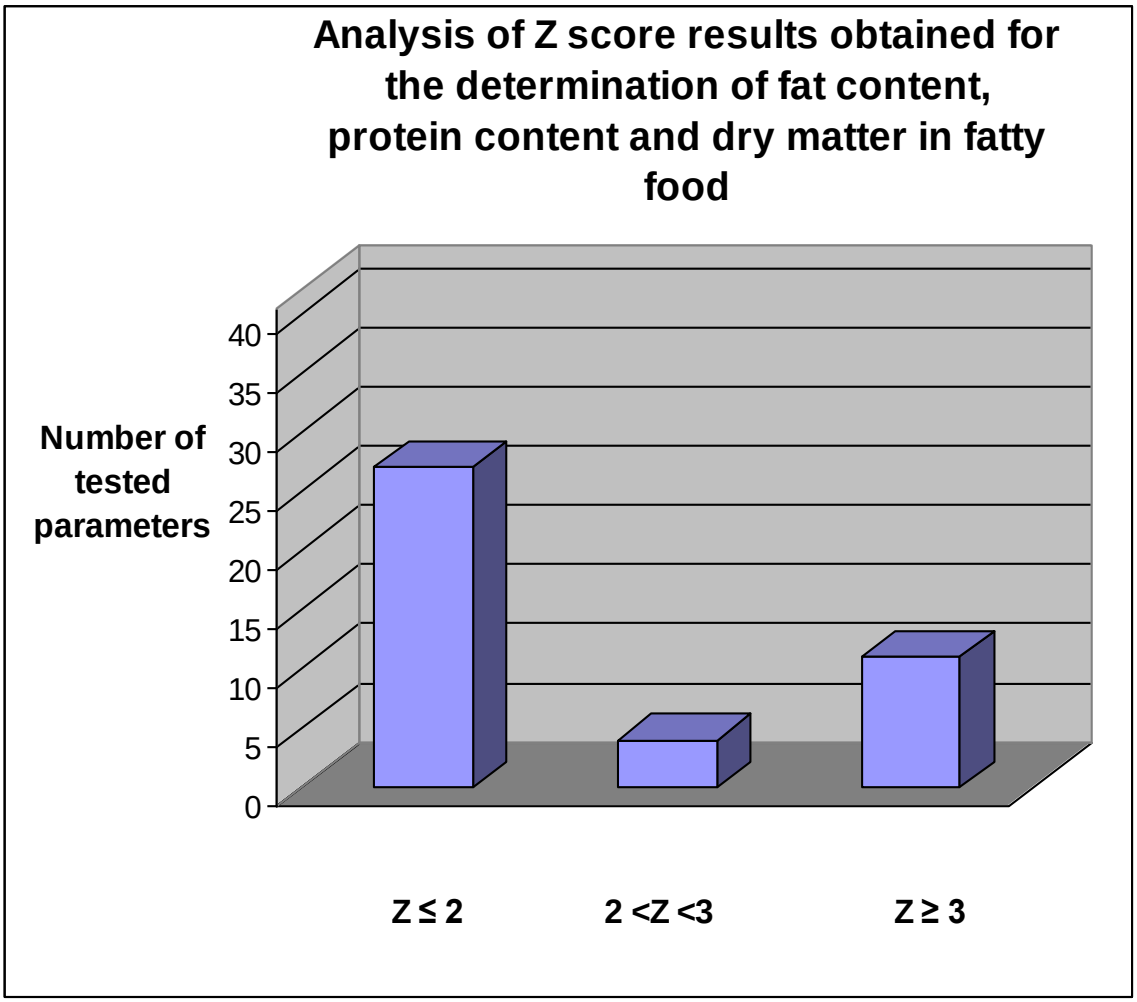


Figure 1

As it is shown in the chart, 27 (64.3 %) of the results have Z score ≤ 2 (satisfactory); 4 (9.5 %) of the results have Z score 2<Z<3 and 11 (26.2 %) of the results have Z score ≥3 (not satisfactory).

The percentage distribution of Z score values is shown in figure 2.

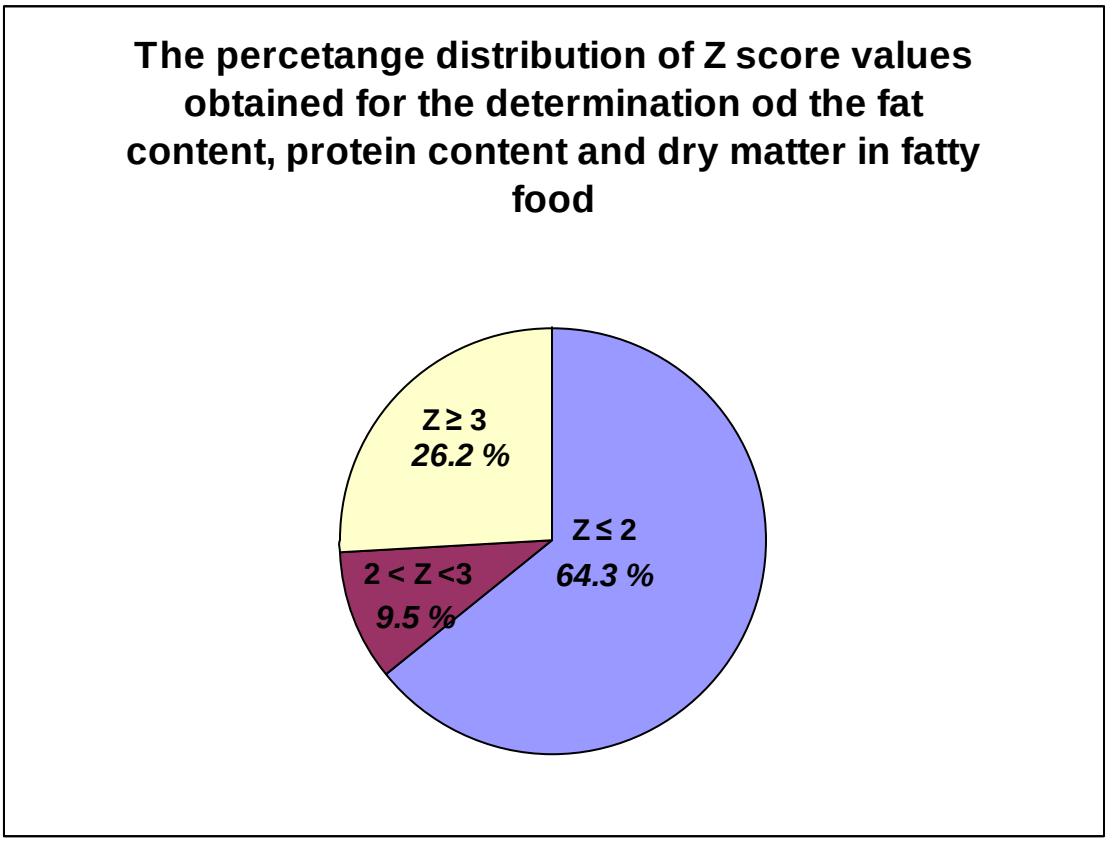


Figure 2

High percentage of total unsatisfactory Z scores (26.2 %) is due to the high Z (Z>3) score obtained for the determination of the fat content in fatty food: coffee cream, cream, powdered milk, yoghurt butter; cheese and powdered milk. The total number of tested samples was 16 (figure 3). 7 measurements were with Z score $Z \leq 2$ (43.75 %), 2 measurements (12.5 %) were with Z score $2<Z<3$ and 7 (43.75 %) measurements were with Z score ≥ 3.

This is due to the systematic errors made during analysis performance as: improper homogenization of the matrix, shorter duration of Soxhlet extraction and errors made during drying and cooling of glassware to constant temperature.

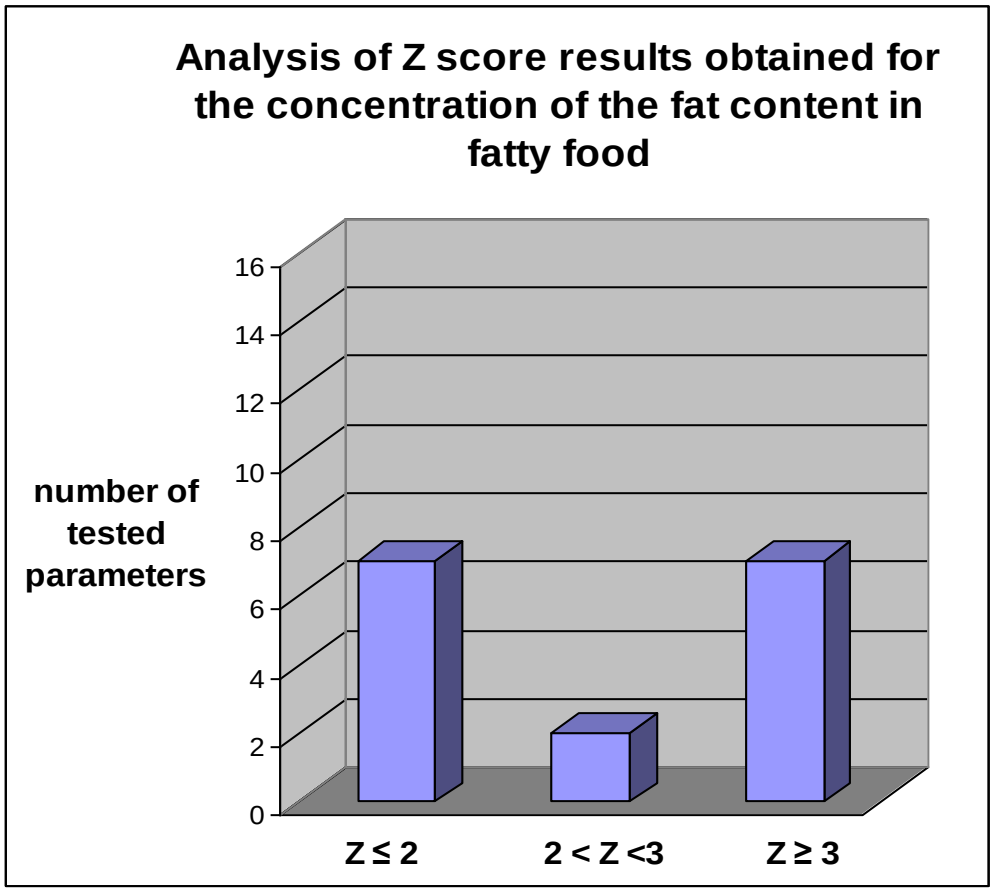


Figure 3

The percentage distribution of Z score values obtained for the determination of the fat content in fatty food as: coffee cream, cream, powdered milk, yoghurt butter; cheese and powdered milk is shown in figure 4.

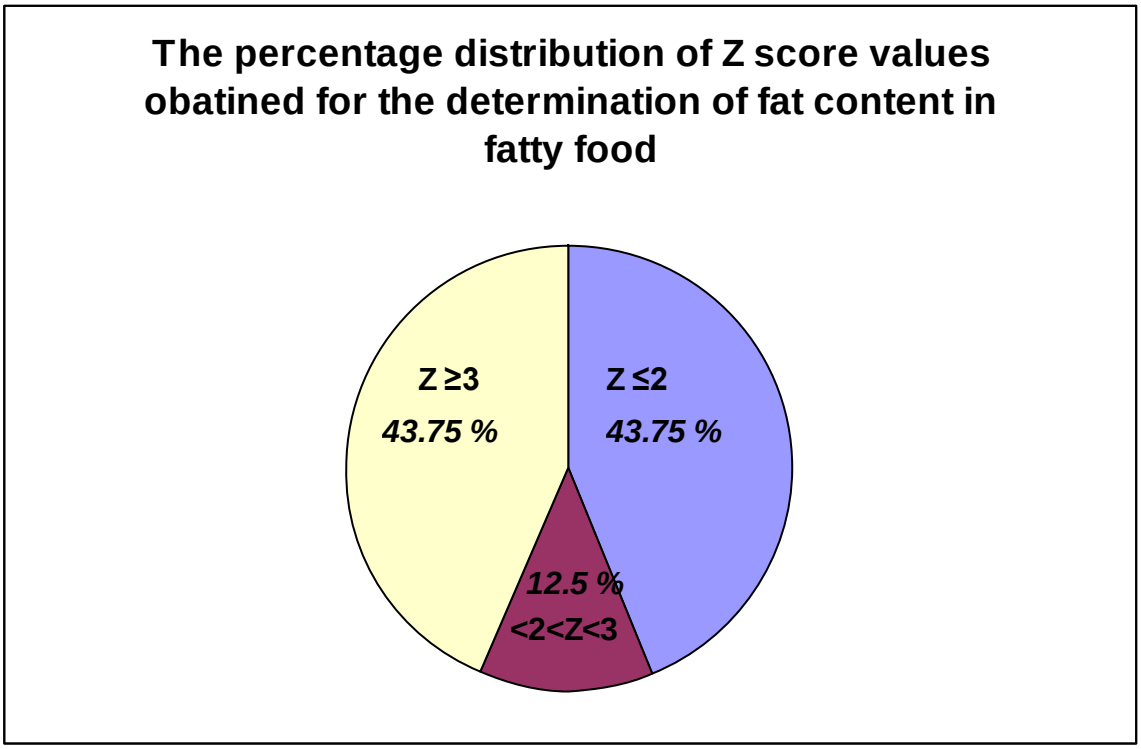

The percentage distribution of Z score values obatined for the determination of fat content in fatty food
Z ≥3
43.75 %
Z ≤2
43.75 %
12.5 %
<2<Z<3

Figure 4

II. ANALYSIS OF ADDITIVES CONTENT AND SOME ROUTINE COMPONENTS IN SOFT DRINKS AND CABBAGE PUREE

Cabbage puree, cola drink, and orange juice were tested on the content of additives (nitrate, benzoic acid, caffeine, K acesulfame, saccharine) and orange juice were tested on the content on citric acid, fructose, glucose, sucrose, total sugars and pH value.

Z score analyses for obtained results of performed measurements are shown in figure 5.

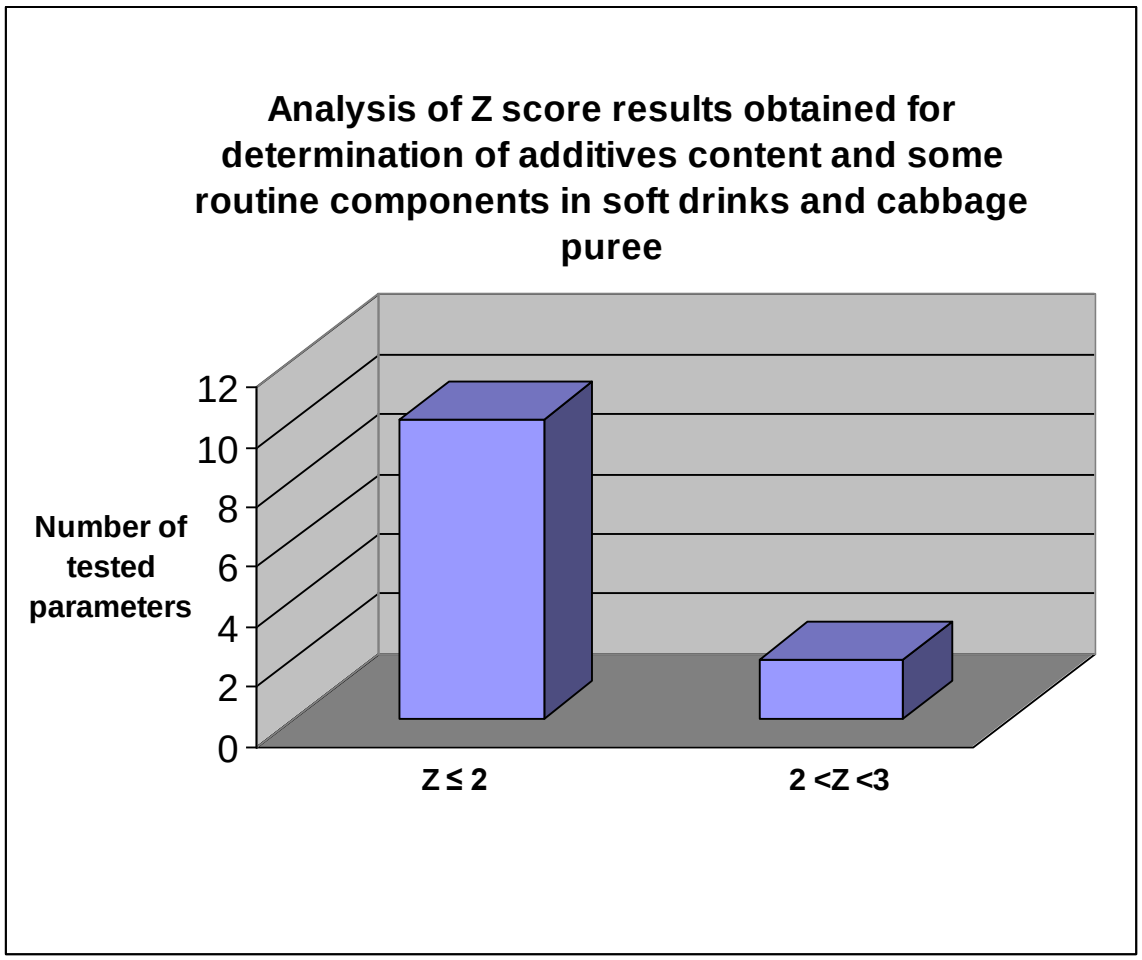


Figure 5

At it is shown in the chart, 10 (83.33 %) of the results have Z score which is satisfactory $Z \leq 2$ and only 2 results have Z score (16.67 %) $2 < Z < 3$. There are not unsatisfactory results with Z score $Z \geq 3$. Total number of tested parameters was 12.

The percentage distribution of Z score values is shown in figure 6.

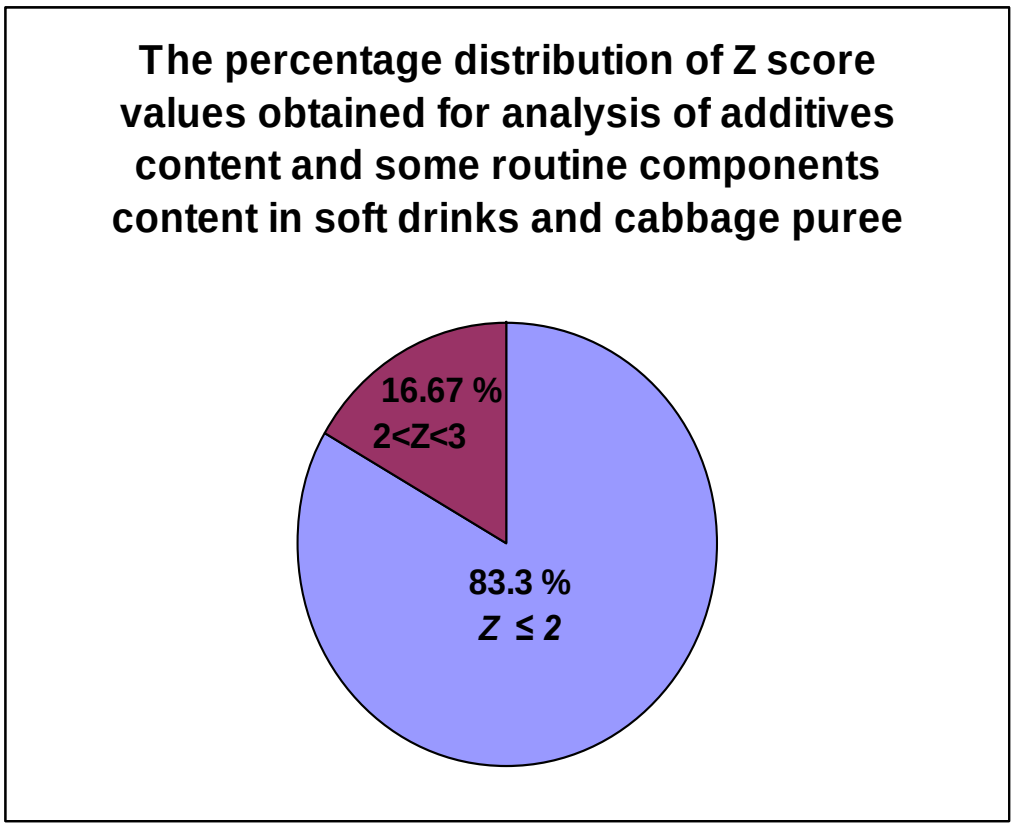

The percentage distribution of Z score values obtained for analysis of additives content and some routine components content in soft drinks and cabbage puree
16.67 %
2<Z<3
83.3 %
Z ≤ 2

Figure 6

III. ANALYSIS OF ORGANOCHLORINE PESTICIDES, ORGANOPHOSPHORUS PESTICIDES AND HERBICIDES IN FOOD AND WATER

Potable water samples, real water samples (spiked), fish oil and maize flour were tested on the content on organochlorine pesticides (endrin; dieldrin; aldrin; pp'DDT; lindane; endosulfan I; endosulfan II; HCH; heptachlor; heptachlor epoxide; cis chlordane and pp'DDE); organophosphorus pesticides (etrimfos; fenitrothion; malathion; pirimiphos–methyl; azinphos-methyl; dichlorvos; chlorofenvinphos; parathion-ethyl; parathion-methyl; chlorpiryfos; diazinon and mevinphos) and herbicides (alachlor; trifluralin; atrazine; propazine and simazine).

Z score analyses for obtained results of performed measurements are shown in figure 7.

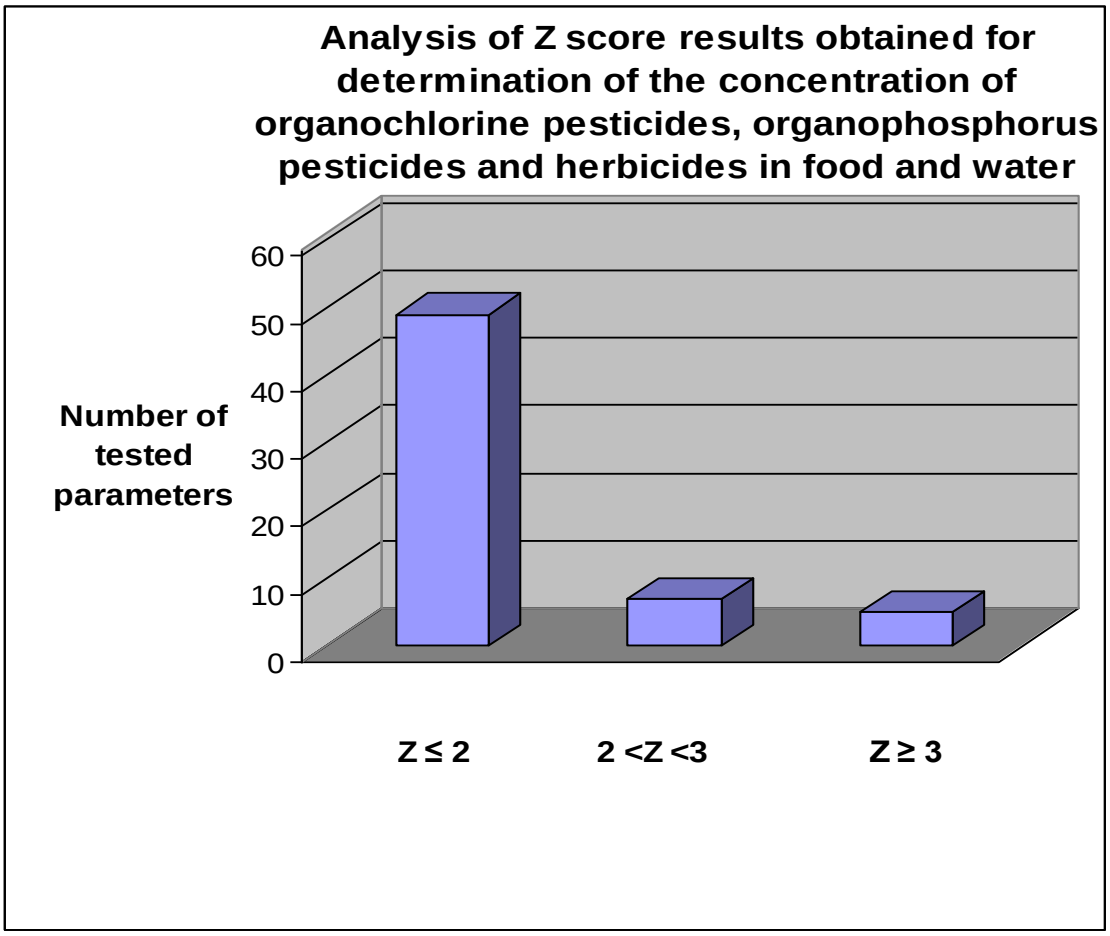


Figure 7

As it is shown in the chart, 49 (80.33 %) of the results have Z score ≤ 2 (satisfactory); 7 (11.47 %) of the results have Z score 2<Z<3 and 5 (8.2 %) of the results have Z score Z≥3 (not satisfactory). Total number of tested parameters was 61.

The percentage distribution of Z score values of tested parameters is shown in figure 8.

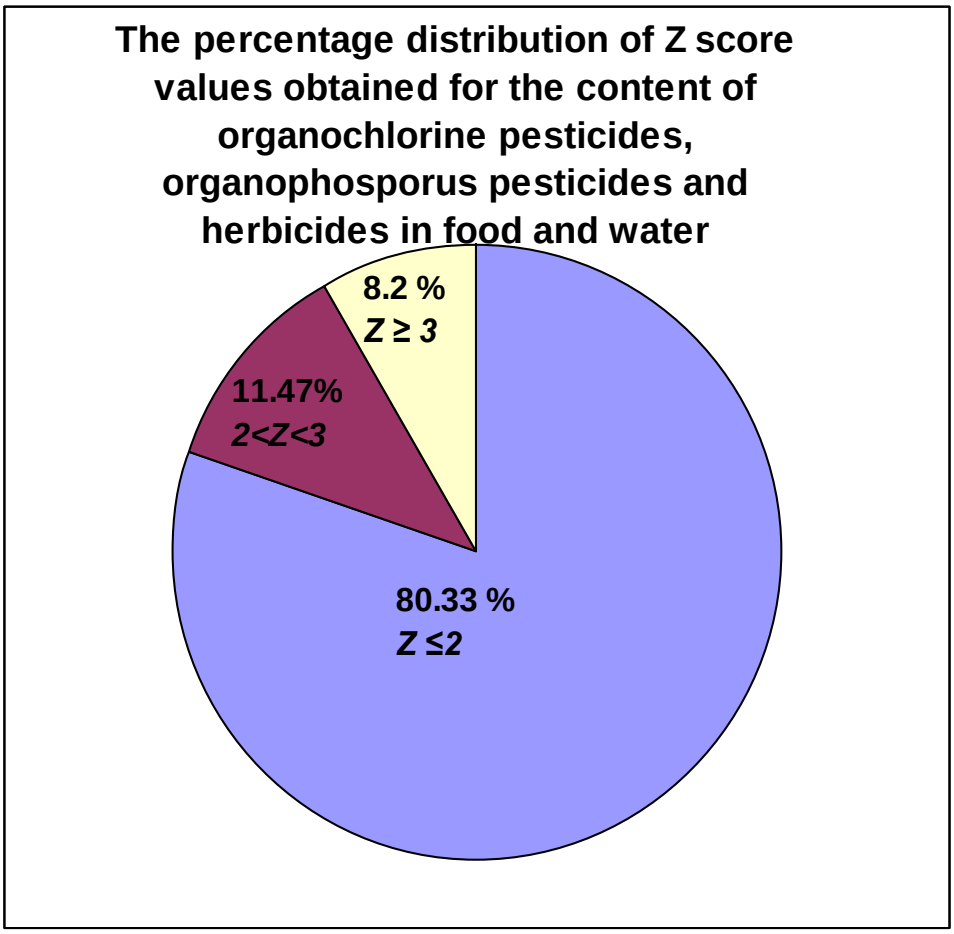

The percentage distribution of Z score values obtained for the content of organochlorine pesticides, organophosporus pesticides and herbicides in food and water
8.2 %
Z ≥ 3
11.47%
2<Z<3
80.33 %
Z ≤2

Figure 8

IV. ANALYSIS OF METALS IN FOOD

Samples of corn flakes, minced canned fish, graham flour, synthetic food of vegetable and animal origin, homogenized canned fruit, powdered rice, dietetic product, fish soup and fresh fish were tested on the content on lead; cadmium; zinc; copper; chromium; iron; manganese; cobalt; nickel; mercury and arsenic.

Z score values obtained for results of performed measurements are shown in figure 9.

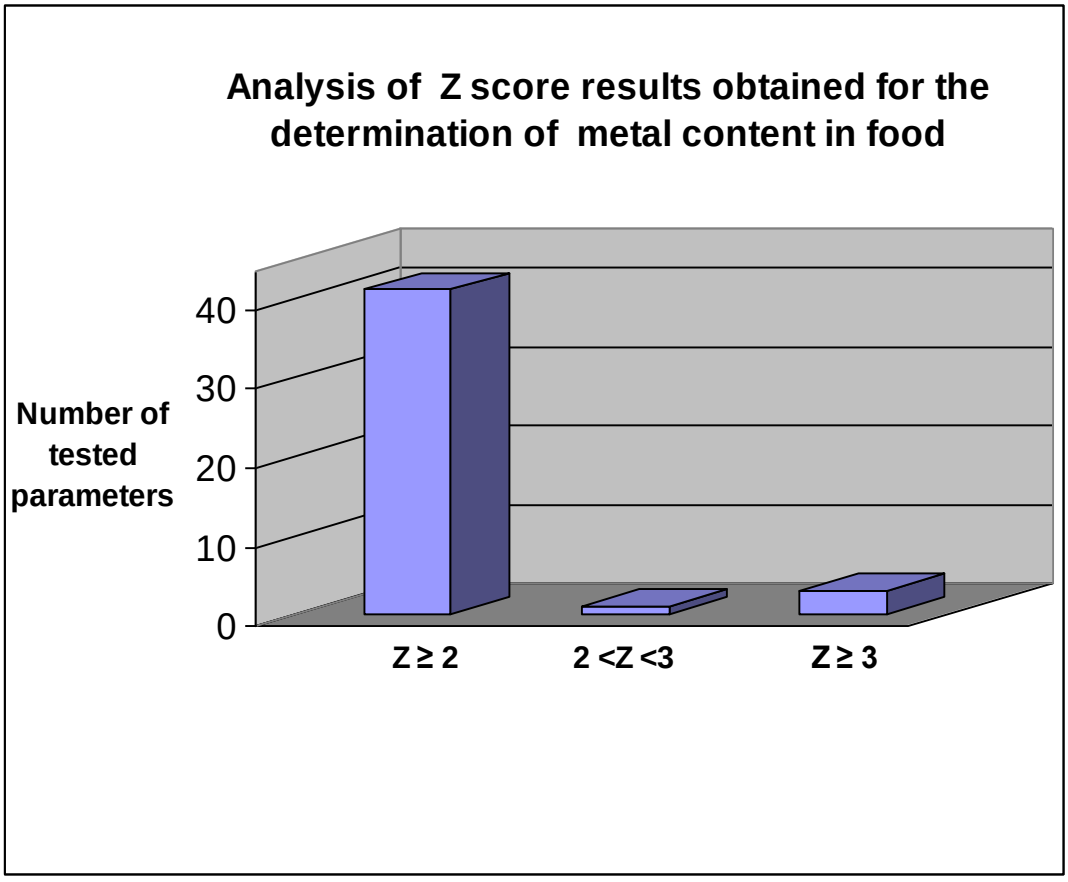


Figure 9

The total number of tested parameters was 45. Satisfactory Z score ($Z \leq 2$) was obtained for 41 of the results (91.1 %), 1 result (2.2 %) has Z score $2<Z<3$ and 3 of the results (6.7 %) have unsatisfactory Z score ($Z \geq 3$).

The percentage distribution of Z score values is shown in figure 10.

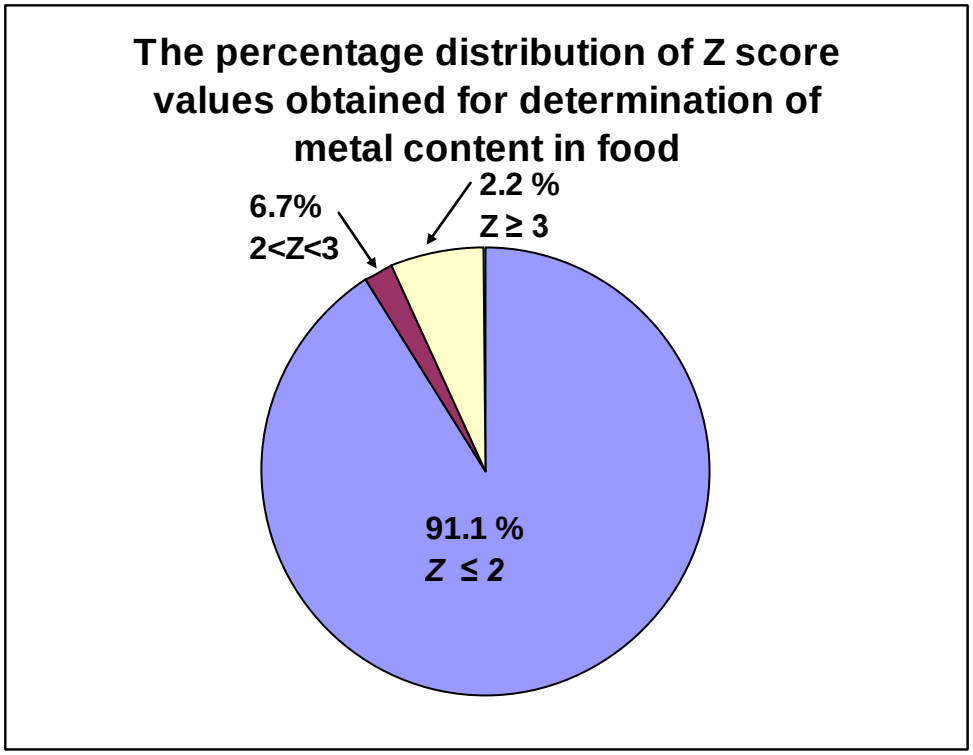

The percentage distribution of Z score values obtained for determination of metal content in food
6.7%
2<Z<3
2.2 %
Z ≥ 3
91.1 %
Z ≤ 2

Figure 10

V. ANALYSIS OF ROUTINE COMPONENTS IN WATER

Potable water samples and real water samples (spiked) were analysed on the following routine components: pH; turbidity; colour; conductivity at 20^0 C; SR phosphate; ammonium; PI; nitrate; nitrite; sulphate; chloride; fluoride; alkalinity; total hardness; calcium; sodium; potassium and magnesium.

Z score analyses for obtained results of performed measurements are shown in figure 11.

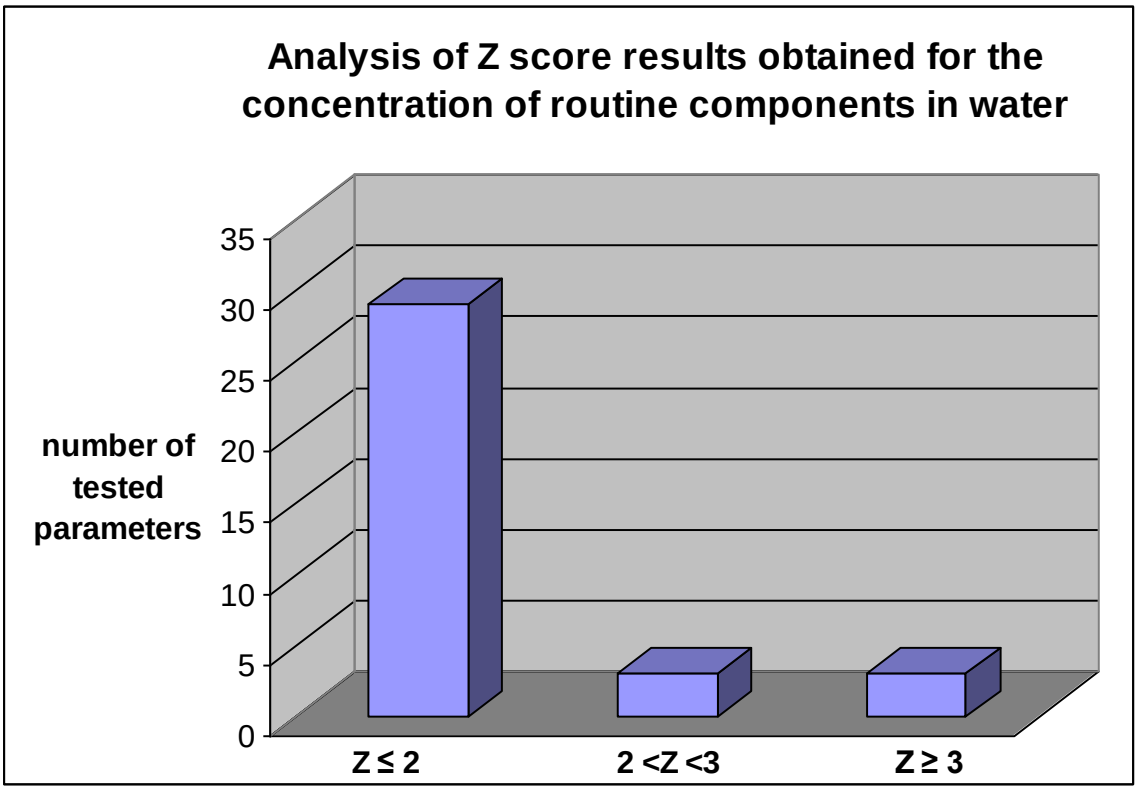


Figure 11

The total number of tested parameters was 35. 29 of tested parameters (82.8 %) have Z score ($Z \leq 2$); 3 (8.6 %) of tested parameters have Z score ($2<Z<3$) and 3 (8.6 %) of tested parameters have unsatisfactory Z score ($Z \geq 3$).

The percentage distribution of Z score values is shown in figure 12.

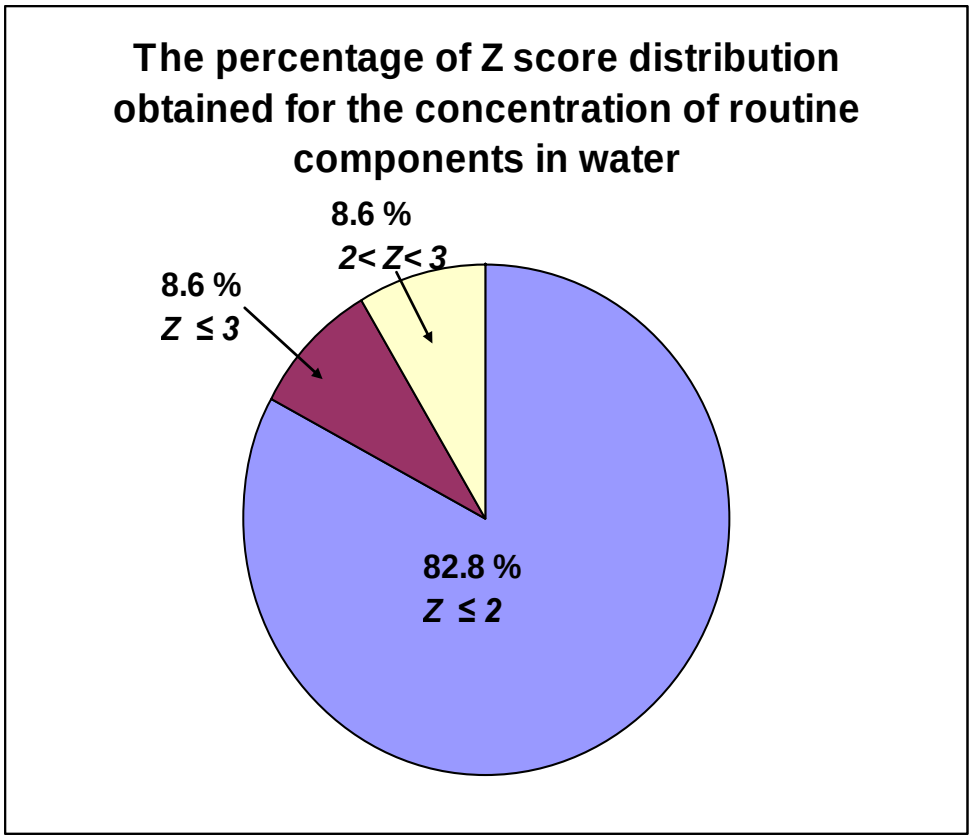


Figure 12

CONCLUSIONS

Laboratories for chemical testing of food and water in Institute of Public Health, Skopje, Republic of Macedonia have an almost one decade participation in various proficiency – testing schemes for 73 different parameters as: fat content, dry matter, water content, benzoic acid, nitrate content, caffeine, saccharine, K – acesulfame., protein content, pH, citric acid, fructose, glucose, sucrose, total sugars, aflatoxins (B1; B2 G1; G2;), trihalomethanes (chloroform; bromoform; carbon tetrachloride; trichloroethene and tetrachloroethene), organophosphorus insecticides (etrimfos; fenitrothion; malathion; pirimiphos–methyl; azinphos-methyl; dichlorvos; chlorofenvinphos; parathion-ethyl; parathion-methyl; chlorpiryfos; diazinon and mevinphos), organochlorine insecticides (endrin; dieldrin; aldrin; pp'DDT; lindane; endosulfan I; endosulfan II; HCH; heptachlor; heptachlor epoxide; cis chlordane and pp'DDE), herbicides (alachlor; trifluralin; atrazine;

propazine and simazine), metals (lead; cadmium; zinc; copper; chromium; iron; manganese; cobalt; nickel; mercury and arsenic), routine components in water (pH; turbidity; colour; conductivity at 20^0 C; SR phosphate; ammonium; PI; nitrate; nitrite; sulphate; chloride; fluoride; alkalinity; total hardness; calcium; sodium; potassium and magnesium). Measurements were performed in 23 different matrixes as: coffee cream, cream, powdered milk, yoghurt butter; cheese; oily dressing, cola drink, cabbage puree, fresh cheese, orange juice, potable water, water real sample, animal feed cereal based, fish oil, maize flour, corn flakes, minced canned fish, graham flour, synthetic food of vegetable and animal origin, homogenized canned fruit, powdered rice, dietetic product, fish soup and fresh fish.

- The total number of tested parameters was 203. 159 (78.32 %) of tested parameters were with satisfactory Z score ($Z \geq 2$); 17 (8.46 %) of tested parameters have Z score ($<2<Z<3$) and 27 (13.3 %) of tested parameters have unsatisfactory Z score ($Z \geq 3$);
- The highest percentage of unsatisfactory Z scores (43.75 %) was obtained for the determination of the fat content in fatty food: coffee cream, cream, powdered milk, yoghurt butter; cheese and powdered milk. This is due to the systematic errors made during analysis performance as: improper homogenization of the matrix, shorter duration of Soxhlet extraction and errors made during drying and cooling of glassware to constant temperature.

- The highest unsatisfactory value for Z score result (Z=128.1) was obtained for gas chromatography determination of trichloroethene in potable water (spiked) with which is a result of lack of individual analytical standard for trichloroethene and use of standard mix instead. In this case there was overlapping of the trichloroethene peak with the peak with other analyte;
- High unsatisfactory Z score values were obtained for the analysis of aflatoxines in animal feed cereal based with TLC chromatography for AFB1 (Z=7.4) and AFB2 (Z=6), which is due of limited separation capabilities of the TLC analytical technique in the case of complex matrixes with a lot of fluorescence impurities.
- The best values for Z score were obtained for the determination of pesticides and herbicides in food and water; determination of metals in food; determination of routine

components in water and determination of additive content and some routine components content in soft drink and cabbage puree. This is a result of the usage of proper analytical method and technique and high quality analytical standards.